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Template-growth of periodically domain-structured KTiOPO_4

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Abstract: We performed the first growth, from a high temperature solution, of a $38.86\text{ }\mu\text{m}$ -periodicity PPKTP crystal of good optical quality over a thickness of more than $800\text{ }\mu\text{m}$ onto each of the two faces perpendicular to the c direction of a PPKTP substrate previously obtained by electric field poling. The quasi-phase matched second harmonic generation properties in the grown layer and substrate are similar and in accordance with calculation.

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OCIS codes: (160.4330) Nonlinear optical materials; (190.2620) Harmonic generation and mixing.

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1. Introduction

Nonlinear optics is increasingly relying on structured materials which allow exploiting quasi-phase matching for maximizing the efficiency of a nonlinear interaction and realizing novel functionality [1-5]. Ferroelectric domain structuring proved to be the most promising technique for fabricating such engineered nonlinear optical materials. Future applications of nonlinear optics will rely on the development of technologies allowing replication and large-scale growth of structured materials using template designs, just as it has occurred in semiconductor electronics. The ferroelectric crystal KTiOPO_4 (KTP) is one of the most promising candidate materials for such an approach, where the finest periodicity ferroelectric domain structures over large volume have been demonstrated [1-7].

Up to now the common method to obtain a periodically poled ferroelectric crystal is by using the electric field poling technique, whereby a local inversion of the spontaneous polarization P_s can be obtained in a single domain crystal by applying an electric field higher than the coercive field to lithographically defined finger electrodes patterned on the polar faces of the crystal. By using this technique the grating periodicity is very well controlled by the lithographic patterning. However, the thickness obtainable is limited in practice by the high voltage necessary, while control of the process and reproducibility in fabricating a high quality domain structure get exceedingly more difficult when the crystal gets larger and thicker.

Periodically poled KTP (PPKTP) is used in quasi-phase matched (QPM) second order nonlinear frequency conversion, like second harmonic generation (SHG) or optical parametric oscillators (OPOs). The QPM nonlinear interactions give unrivalled degree of design freedom and can be substantially more efficient than birefringence phase-matched ones due to the possibility to access to the largest diagonal nonlinear coefficient [8]. Although 3-mm-thick KTP crystals have been poled, a variation in stoichiometry in presently available wafers is the primary difficulty in getting thick poled crystals, especially for dense gratings [7]. So far QPM materials are perceived as applicable only to relatively low-energy applications due to limitations in the optical aperture sizes which can be reliably reproduced.

An *in situ* growth technique has been proposed in order to obtain larger size PPKTP samples from single domain KTP crystals [9], but unfortunately the regularity of the obtained grating period was not sufficient for a use in practical nonlinear devices. The same limitation occurred during the attempts to *in situ* grow periodically-poled LiNbO_3 , another ferroelectric crystal widely used for QPM [10]. Note also that for the non-ferroelectric crystal GaAs, an

epitaxial growth method has been used for the fabrication of orientation-patterned GaAs (OPGaAs) films suited for nonlinear optical frequency conversion [11,12].

Here we demonstrate a technology for growth of periodically domain-structures of KTP from a template, leading to scalability of the nonlinear optical structures to large volumes. This new process enables high-quality crystal growth below the Curie temperature and below the roughening temperature of the polar faces, thereby preserving an excellent crystal morphology and ferroelectric domain structure.

2. Description of the new process

With the aim of increasing the size of PPKTP crystals with a controlled and regular grating period, we developed an epitaxial growth process using seeds made of thin PPKTP plates previously obtained by electric field poling. For the following, we keep the denomination “PPKTP” for the grown periodically domain-structured KTP crystal. The poling step (Step I in Fig. 1) requires a sample exhibiting (001) and (00 $\bar{1}$) crystal faces, so that the growth step (Step II Fig. 1) has to be performed onto this face. This constraint is a first difficulty to circumvent as this face is not present in the standard equilibrium morphology. The growth temperature of PPKTP is also imposed by the ferroelectric character of the crystal, since it is necessary to “build” the crystal below its Curie temperature in order to avoid unwanted erasure of the domain grating. By using a high temperature solution method, the so-called “flux method”, and by choosing an appropriate chemical composition of the flux solution, it is then possible to meet both these constraints.

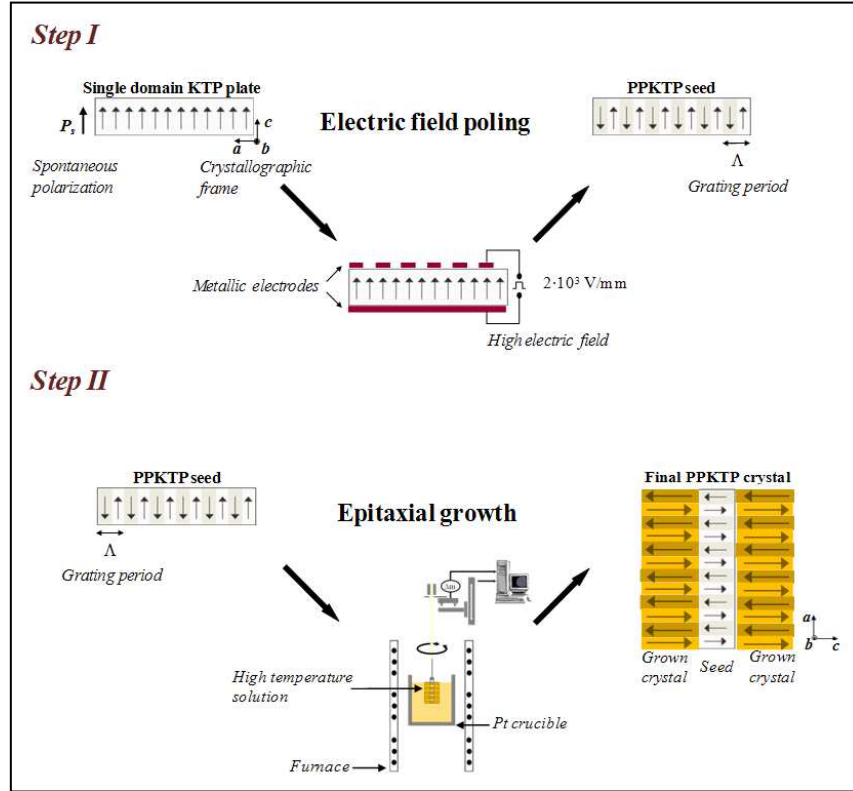


Fig. 1. Scheme of the process showing the different steps to obtain large size PPKTP crystals. Step I corresponds to the fabrication of a PPKTP sample from a single domain KTP plate by electric field poling. Step II corresponds to the growth of a large size PPKTP crystal from the PPKTP seed by the flux method.

3. Definition of the growth conditions

KTP crystallizes in the orthorhombic system and belongs to the acentric point group $mm2$ with the space group $Pna2_1$ at room temperature [13], the c axis being along the direction of the spontaneous polarization P_s [14]. KTP has a ferroelectric phase transition with the change of symmetry $Pna2_1$ (acentric) – $Pnam$ (centric) at the Curie temperature T_c [15]. This sets an upper temperature for growth of KTP in its ferroelectric phase. It has been shown that T_c can vary between 1193 K and 1233 K as a function of the flux growth conditions of KTP and this is directly correlated to the stoichiometry, where the higher temperature corresponds to a more stoichiometric crystal: T_c increases as a function of the molar ratio K/P while it decreases as a function of the growth temperature for a given ratio K/P [16]. This fact has to be taken into account in order to design the right flux.

The standard morphology of KTP as obtained by flux growth around 1100 K is depicted in Fig. 2(a). It does not exhibit (001) and (00 $\bar{1}$) faces, the crystal faces orthogonal to the c axis [17,18]. However, these faces, of so-called non standard morphology, shown in Fig. 2(b), exist only when the growth is performed below their roughening temperatures, *i.e.* $T_R \approx 1053$ K. The roughening temperatures relative to several faces of KTP as calculated from the Rijpkema model [19], are given in Fig. 2(c) for comparison. Note that the morphology of a KTP crystal grown by the hydrothermal method does not exhibit (001) faces at all, even if the growth is performed below the roughening temperature [20]. It may be due to a higher growth rate of (001) faces compared with those of the neighbor faces {201} and {011}. However, by using a $K_6P_4O_{13}$ solvent and high amounts of PbO [21], it is possible to obtain (001) faces at a temperature higher than T_R . This is an interesting approach but here we preferred to consider fluxes with a lower toxicity.

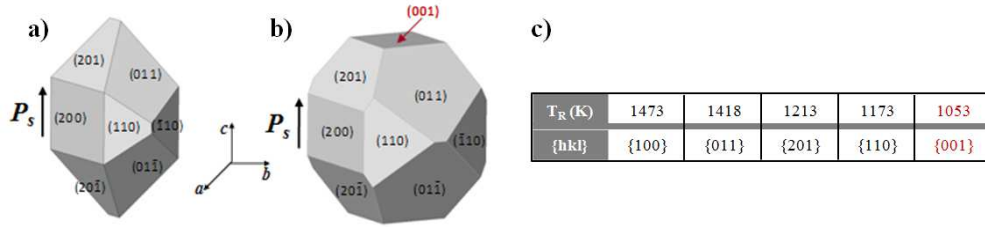


Fig. 2. (a) Standard morphology of KTP crystals. (b) The morphology of KTP exhibiting (001) and (00 $\bar{1}$) faces. (c) Roughening temperatures, T_R (K), of different {hkl} faces.

By using a standard KTP crystal, it is first necessary to cut (001) and (00 $\bar{1}$) faces in order to realize the electric field poling (Step I of Fig. 1). The growth stage of the process (Step II of Fig. 1), following the poling stage, has hence to be performed onto (001) and (00 $\bar{1}$) faces. If Step II is realized at a temperature higher than the roughening temperature of (001) faces, a capping process would take place leading to a detrimental reconstruction with a pyramidal domain shape formed by {201} and {011} faces [22]. The flux composition is then a key point in performing the growth of domain structured KTP, so that the temperature can be kept below the Curie temperature and below the roughening temperature of the (001) faces. The commonly used flux for growing KTP is $K_6P_4O_{13}$, but the lower limit of growth is 1098 K [17,18], due to the formation of a neighboring polyphosphate complex phase below this temperature [23].

Here we propose to use a flux containing a mixture of KPO_3 and KF from which KTP can be obtained at temperatures as low as 873 K, corresponding to the eutectic point of the system [24]. This increased temperature range compared with the solvent $K_6P_4O_{13}$ is due to a higher ionic character of the solution, thanks to the presence of KF that prevents the formation of undesired polyphosphate complex phases. Knowledge of the equilibrium curve is required in order to define the composition of the halide flux enabling the growth to be performed at the

required temperature. We considered the same molar ratio as in the case of $\text{K}_6\text{P}_4\text{O}_{13}$, *i.e.* $\text{K}/\text{P} = 1.5$, to be able to use the experimental data previously measured using $\text{K}_6\text{P}_4\text{O}_{13}$ [25]. The corresponding reaction constant as a function of temperature was deduced by using an ionic solubility model [26,27]. It allowed us to determine the molar enthalpy of crystallization, *i.e.* $\Delta H = 6001.5$ cal/mol, from which finally the equilibrium curve of Fig. 3 was calculated. Note that the figure contains equilibrium curves for two solvents, but they overlap since they correspond to the same K/P ratio. We validated the calculations by a thermo-gravimetric measurement of the saturation temperature corresponding to the molar composition $0.1 \text{ KTP} - 0.6 \text{ KPO}_3 - 0.3 \text{ KF}$: we found 1005.5 ± 0.1 K, which is very close to the theoretical value, *i.e.* 1003 K, as shown in Fig. 3.

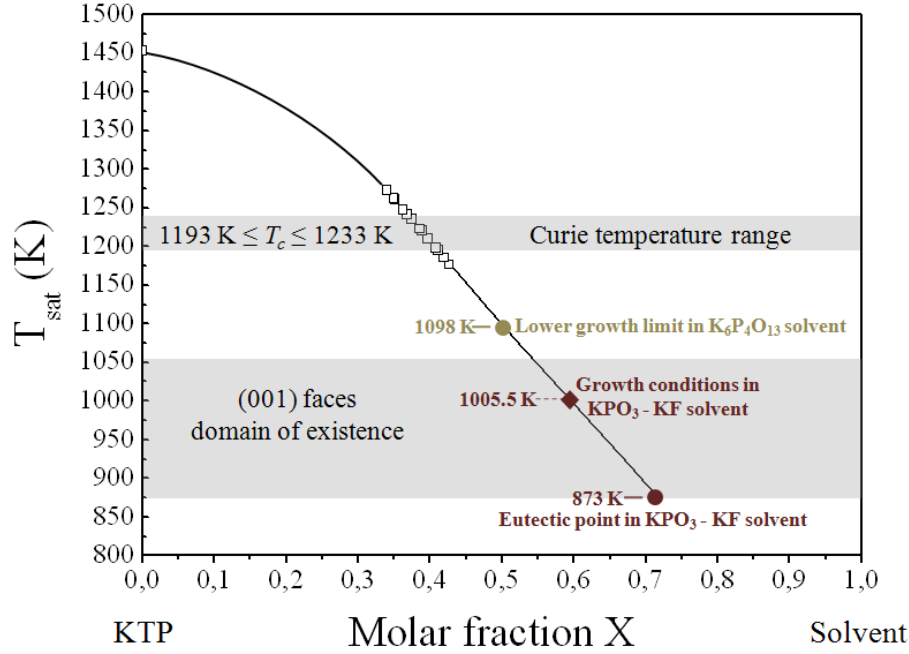


Fig. 3. The pseudo-binary phase diagram of KTiOPO_4 (KTP) using $\text{K}_6\text{P}_4\text{O}_{13}$ and $4\text{KPO}_3 : 2\text{KF}$ solvents. T_{sat} is the saturation temperature of KTP below which the crystallization can occur; X is the molar fraction defined by $[\text{K}_6\text{P}_4\text{O}_{13}]/\{[\text{KTP}] + [\text{K}_6\text{P}_4\text{O}_{13}]\}$ or $[4\text{KPO}_3 : 2\text{KF}]/\{[\text{KTP}] + [4\text{KPO}_3 : 2\text{KF}]\}$ according to the considered solvent.

4. Crystal growth

In a preliminary step, the morphology was checked on small size single domain KTP crystals grown by spontaneous nucleation from the halide solvent exhibiting different saturation temperatures that were predicted using the equilibrium curve of Fig. 3. The grown crystals exhibited (001) faces below 1048 K, which is very close to the calculated roughening temperature of 1053 K. Furthermore, we performed epitaxial growth experiments onto polished (001) and $(00\bar{1})$ faces of a single domain KTP crystal. The flux composition $0.1 \text{ KTP} - 0.6 \text{ KPO}_3 - 0.3 \text{ KF}$ previously considered was used since the corresponding saturation temperature is below the roughening temperature of (001) faces. We applied an over-saturation of 2.2 % corresponding to growth 6 degrees below the saturation temperature. During growth the single domain KTP seed was rotated with an angular speed of 30 rpm. By using a scanning electron microscope (SEM), we verified a very high quality of the interface between the seed and the epitaxially grown layer.

In a second step, we performed epitaxial growths of PPKTP onto (001) and (00 $\bar{1}$) faces (Step II in Fig. 1) of PPKTP plates with the dimensions of 11 mm x 6 mm x 1 mm ($a \times b \times c$) where a central area of 7 mm x 3 mm x 1 mm had previously been periodically inverted with a grating period of $\Lambda = 38.86 \mu\text{m}$, by electrical poling (Step I of Fig. 1). The flux composition 0.1 KTP – 0.6 KPO₃ – 0.3 KF as previously defined was used, and a constant cooling ramp of 0.05 K/h, starting from 1005.5 K, was applied. Thicknesses of the domain structured KTP layers up to 800 μm were grown onto each of the two c faces, *i.e.* the (001) and (00 $\bar{1}$) faces. An example of such a sample is shown in Fig. 4(a). By using a scanning electron microscope (SEM), we were able to verify the very high interface quality, as shown in Fig. 4(b), and a propagation of the domains over a thickness 225 μm without any crack or variation of the domains size as indicated by Fig. 4(b) and (c). The domains still propagate from 225 μm until the boundaries of the grown layers but with some cracks and inclusions.



Fig. 4. Periodically domain-structured-KTP films grown on a PPKTP in a flux with the composition 0.1 KTP – 0.6 KPO₃ – 0.3 KF. **a)** Picture of a PPKTP crystal and the corresponding orientation used for the growth. **b)** SEM image along the b axis of the grown layer and seed. **c)** SEM image along the c axis of the grown layer at 225 μm far from the surface of one side of the seed.

Note that due to the possibility to grow layers on both sides of the seed simultaneously, it is possible to get double volume compared with the usual single layer growth.

5. Optical characterization

In order to check the optical quality of the grown layer in terms of the domain grating regularity, we performed first order QPM SHG measurements with the beam propagating along the a axis and probing the d_{33} coefficient of the crystal, the SH and fundamental waves being polarized along the c axis. The SH intensity was measured as a function of the fundamental wavelength λ_ω at different depths in both the seed and epitaxial layer at room temperature. The $1/e^2$ diameter of the fundamental beam was 70 μm , which enabled an appropriate spatial resolution for scanning over the whole thickness of the sample. In Fig. 5 two typical examples of measurements are shown that show the equivalence in the nonlinear optical performance of the seed and epitaxial layer. The quasi-phase matching peak was $2126.9 \pm 0.5 \text{ nm}$ in the epitaxial layer, which is very close to what was measured in the seed, *i.e.* $2127.1 \pm 0.5 \text{ nm}$, showing the resemblance between the two regions. The spectral acceptance was the same in the seed and in the epitaxial layer, *i.e.* $L\delta\lambda_\omega = 12.7 \text{ nm.cm}$, which attests that the corresponding periodically poled regions have the same extension along the a axis and that the grown layer faithfully reproduces the seed. The acceptance bandwidth is very close to the one calculated for a perfect structure, *i.e.* $L\delta\lambda_\omega = 9.4 \text{ nm.cm}$, which further demonstrates the high quality of the grown layer. The peak amplitude of the SH intensity is about 28% smaller in the grown layer than in the seed, corresponding to slightly higher losses due to scattering. The defects density increases up to 225 μm as mentioned above in section 4, which is detrimental for optical measurements.

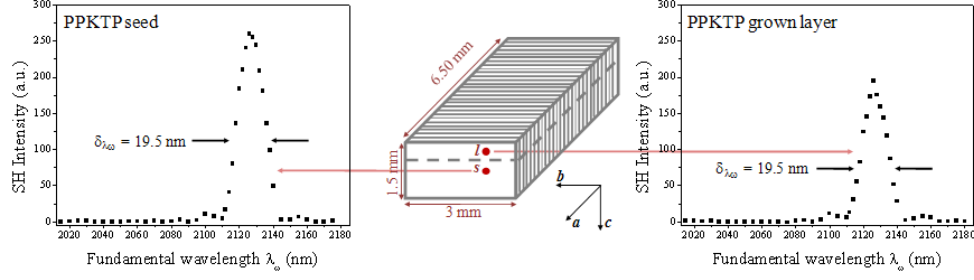


Fig. 5. Comparison between the quasi-phase matched second harmonic generation (QPM SHG) properties of the seed and one side of the grown layer at room temperature. QPM SHG measurements performed at two different depths, 275 μm in the seed (s) and 225 μm in the epitaxial layer (l) measured from the interface (dashed line) in a sample with a grating periodicity $\Lambda = 38.86$ μm .

5. Conclusions

In summary, periodically domain-structured KTP layers with thicknesses up to 800 μm and regular periodicity onto (001) and (00 $\bar{1}$) faces of the initial PPKTP seed have been obtained for the first time by epitaxial growth. The use of a $4\text{KPO}_3 : 2\text{KF}$ solvent allowed the growth to be performed below T_c and the roughening temperature of the (001) face. Up to now, the crystalline quality is perfect over 225 μm , which allowed us to perform quasi-phase matched second harmonic generation experiments within the corresponding volume. By this way, we demonstrated that the grown layer and the seed are very similar, which shows that this technology well meets the requirement for template-growth of engineered PPKTP or other nonlinear structures. The current experiments aim at increasing the crystal quality above 225 μm .

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